Critical and Tricritical Behavior at the Nematic to Smectic-*A* Transition

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High-resolution x-ray scattering measurements of the nematic to smectic-*A* transitions in two different homologous series are reported; it is found that the correlation-length exponents $\nu_{\parallel}$ and $\nu_{\perp}$ and the susceptibility exponent γ decrease continuously with decreasing nematic range; the transitions ultimately become first order. The exponents at the crossover point are close, but not identical, to mean-field tricritical values. For both series and all samples $\nu_{\parallel} \neq \nu_{\perp}$ while $\alpha + \nu_{\parallel} + 2\nu_{\perp} - 2 = 0$ to within the errors.

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Tricritical behavior,[1] in which a phase transition crosses over from being second to first order, has now been studied extensively in a variety of systems including He^3-He^4 mixtures[2] and metamagnets such as $FeCl_2$ and $Dy_3Al_5O_{12}$.[3] In general it is found that the tricritical region is well described by mean-field theory as expected on the basis of Ginzburg-criterion and renormalization-group arguments.[4] Alben[5] has predicted that a He^3-He^4-like tricritical point may occur in binary liquid crystal mixtures for the nematic to smectic-*A* (N-S_A) transition. So far very little information is available on N-S_A tricritical behavior except from some heat-capacity measurements by Brisbin *et al.*[6] in the homologous series pentylbenzenethioalkoxybenzoate ($\overline{n}$S5) and by Thoen and co-workers[7] in the series alkoxycyanobiphenyl (nCB). In this letter we report detailed studies using high-resolution x-ray scattering techniques of the phase-transition behavior in these two homologous series with emphasis on the tricritical region.

Studies of N-S_A tricritical behavior are important both because of intrinsic interest in tricritical phenomena and because of the possible light they can shed on the general N-S_A problem. Alben's analogy with He^3-He^4 mixtures was based on the McMillan–Kobayashi–de Gennes (M-K-deG) model[8] in which the N-S_A transition is in the universality class of a superconductor ($d = 3$, $n = 2$) albeit with an anisotropic gauge. The tricritical behavior which occurs with decreasing nematic range is driven by the coupling between the nematic and smectic order parameters. There is an important difference between the binary liquid crystal mixture and He^3-He^4 cases in that in the former the concentration represents the nonordering field whereas in the latter it represents the nonordering density. Unfortunately, the elegant M-K-deG analogy to superconductivity does not properly describe the empirical behavior. Specifically, the longitudinal and transverse correlation lengths diverge at different rates.[9] This may be due to the crossover effect discussed by Lubensky and co-workers[10] in which $\nu_{\perp}$ should evolve from $\nu_{\parallel}$ to $\nu_{\parallel}/2$ as T_{NA}, the N-S_A transition temperature, is approached. In addition, the power laws for all measured quantities exhibit nonuniversal behavior with exponents depending on the McMillan ratio[8] T_{NA}/T_{NI}, where T_{NI} is the N-isotropic transition temperature.[9] Further, for no value of T_{NA}/T_{NI} do all of the measured exponents agree with the $d = 3$, $n = 2$ values. Recently Brisbin *et al.*[6] and Garland *et al.*[9] have postulated that these continuously varying exponents represent a smooth crossover from critical to tricritical behavior, although the tricritical region itself has not yet been properly explored. In order to test these ideas and to elucidate the N-S_A problem as a whole we have studied in detail this critical-tricritical crossover.

As noted above, experiments were carried out in the two homologous series $\overline{n}$S5 and nCB. By mixing neighboring homologs one can effectively vary n continuously. Heat-capacity experiments[6,7] suggest that the tricritical point occurs for $n \simeq 10$ for $\overline{n}$S5 and $n \simeq 9$ for nCB. The nCB material was purchased from British Drug House and used as received while the $\overline{n}$S5 compounds were synthesized by one of us (M.E.N.).[11] The x-ray experiments involved standard techniques in our laboratory.[12] A longitudinal in-plane resolution of $\sim 5\times10^{-4}$ Å^{-1} or $\sim 1\times10^{-4}$ Å^{-1} half width at half maximum (HWHM) was achieved by employing

perfect Ge(111) or Si(111) crystals as monochromator and analyzer using Cu $K\alpha$ radiation. The transverse resolution in the vertical direction was ~ 0.02 Å^{-1} HWHM while the transverse in-plane resolution was essentially perfect.

The samples were contained in beryllium-window cells placed in a two-stage oven. The director was aligned by an 8-kG magnetic field. In these measurements we defined T_{NA} as the temperature at which the longitudinal scan first became resolution limited; using this criterion T_{NA} could be determined to within 2×10^{-3} °C.

In the nematic phase, the critical scattering is centered about the points $(0,0,\pm q_{\parallel}{}^{0})$. It has been found previously[12] that the scattering is well represented by the form

$$\sigma(\vec{q}) = \frac{\sigma_0}{1+\xi_{\parallel}{}^2(q_{\parallel}-q_{\parallel}{}^0)^2+\xi_{\perp}{}^2q_{\perp}{}^2(1+C\xi_{\perp}{}^2q_{\perp}{}^2)} \quad (1)$$

convoluted with the instrumental resolution function. Thus from scans through $(0,0,q_{\parallel}{}^{0})$ along q_z and q_x it is possible to measure σ_0, $\xi_{\parallel}$, and $\xi_{\perp}$.

We show in Fig. 1 values for $\xi_{\parallel}$ obtained in this fashion for a series of $\overline{n}$S5 samples. For concentrations exhibiting a second order N-S_A transition each of $\xi_{\parallel}$, $\xi_{\perp}$, and σ_0 exhibit single power-law behavior over the reduced temperature range ~ 10^{-2} to ~ 5×10^{-5}. However, if the transition is first order then T_{NA}, defined by the appearance of a resolution-limited smectic peak, should be too high and accordingly the data should saturate at small reduced temperatures. Such an effect is indeed observed for $\overline{10.2}$S5 and $\overline{10.4}$S5, suggesting that these samples exhibit first-order N-S_A transitions. Thus to within our accuracy we find that the N-S_A tricritical point for the $\overline{n}$S5 series occurs for $n = 10 \pm 0.2$. This is consistent with the heat-capacity measurements of Brisbin *et al.*[6] We find quite similar results in the nCB series; in that system we find the tricritical point for $n = 9.0 \pm 0.1$; this agrees to within the errors with the heat-capacity study by Thoen and co-workers.[7] The corresponding McMillan ratios for $\overline{n}$S5 and nCB are 0.984 and 0.994, respectively.

We now discuss the power laws observed for each series. It is evident from Fig. 1 that both the critical exponents and absolute lengths decrease dramatically as the tricritical concentration is approached. Nevertheless, single power laws describe the data quite well over the complete temperature range. Similar results hold for $\xi_{\perp}$ and σ_0 in both the $\overline{n}$S5 and nCB series. The results at the tricritical concentrations are shown in Fig. 2. Again single power laws work

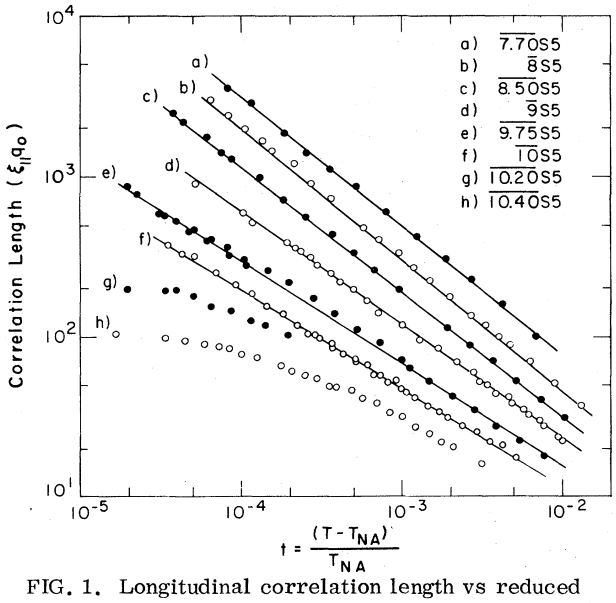

FIG. 1. Longitudinal correlation length vs reduced temperature for $\overline{n}$S5. The solid lines are single power-law fits. Deviations from a single power law for $\overline{10.2}$S5 and $\overline{10.4}$S5 are characteristic of first-order behavior. The data for $\overline{7.7}$S5 and $\overline{8}$.S5 were taken by C. R. Safinya (unpublished).

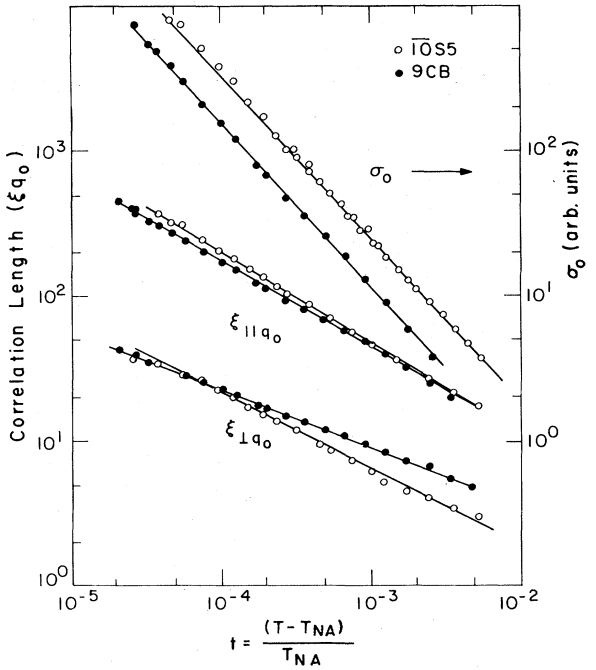

FIG. 2. Susceptibility and the longitudinal and transverse correlation lengths vs reduced temperature for 9CB and $\overline{10}$S5. The solid lines are single power fits. The susceptibility amplitude difference between the two samples is for display purposes only.

well over the reduced temperature range $\sim 2 \times 10^{-5}$ to 8×10^{-3} except possibly for $\xi_\perp$ in 9CB. One of the most surprising features is that the absolute lengths for $\overline{10}$S5 and 9CB are closely similar, suggesting universal behavior. For $\overline{10}$S5 we find $\gamma = 1.10 \pm 0.05$, $\nu_\parallel = 0.61 \pm 0.03$, and $\nu_\perp = 0.51 \pm 0.05$ while in 9CB $\gamma = 1.10 \pm 0.05$, $\nu_\parallel = 0.57 \pm 0.03$, and $\nu_\perp = 0.37^{+0.07}_{-0.03}$. These may be compared with the mean-field tricritical values[4] $\gamma = 1$, and $\nu_\parallel = \nu_\perp = 0.5$. The measured exponents are close to these values although the discrepancies are significant. These results and those for several other compounds in the series are given in Table I. It has been found previously that the anisotropic hyperscaling relation

$$\alpha + \nu_\parallel + 2\nu_\perp = 2 \qquad (2)$$

holds quite well for the N-S_A transitions away from the tricritical point. As shown in Table I, for $\overline{10}$S5, $\alpha + \nu_\parallel + 2\nu_\perp = 2.08 \pm 0.18$, while for 9CB, $\alpha + \nu_\parallel + 2\nu_\perp = 1.84^{+0.22}_{-0.14}$. Thus Eq. (2) is satisfied to within the errors at the N-S_A tricritical point as well. Finally, in previous studies of N-S_A transitions[9] it has been found that $\nu_\parallel - \nu_\perp = 0.13 \pm 0.03$. For $\overline{10}$S5 and 9CB we find $\nu_\parallel - \nu_\perp = 0.10$ and 0.20, respectively, consistent with previous results.

These experiments thus have dramatically confirmed the suggestion of Brisbin *et al.*[6] and Garland *et al.*[9] that there is a continuous evolution of the measured exponents for N-S_A transitions from the saturated, that is, the long nematic range, limit to the tricritical region. Somewhat ironically, all of the systems studied in the first-generation N-S_A experiments were in the middle of this critical to tricritical crossover region.[9] We now discuss the exponents themselves. As discussed earlier, in the M-K-deG model[8] the exponents should cross over from those characteristic of the $d = 3$, $n = 2$ universality class, $\gamma = 1.32$, $\nu_\parallel = \nu_\perp = 0.67$, $\alpha = -0.03$, to the tricritical mean-field values $\gamma = 1$, $\nu_\parallel = \nu_\perp = 0.5$, $\alpha = 0.5$. However, the model neglects the divergent phase fluctuations characterizing the smectic-A phase. Lubensky and co-workers[10] have treated the phase fluctuations by making a gauge transformation to an order parameter with nondivergent fluctuations and then, after making an appropriate decoupling approximation, transforming back to the laboratory gauge. This model predicts that the measured $\xi_\parallel$ should scale like $\tau^{-\nu_\parallel}$ over the accessible temperature range whereas $\xi_\perp$ should exhibit a crossover from $\tau^{-\nu_\parallel}$ to $\tau^{-\nu_\parallel/2}$. For the $d = 3$, $n = 2$ critical behavior this also necessitates that the appropriate hyperscaling expression is $\alpha + 3\nu_\parallel = 2$, *not* Eq. (2). Similar predictions have recently been given by Grinstein and Toner[13] using a different approach.

In the context of butyloxybenzlideneheptylaniline (4O.7), it has been shown[9] that the crossover form is capable of accounting for the measured $\xi_\perp$; a single power law seems to work slightly better for $\xi_\parallel$ but the differences between the crossover and single power-law forms are within the overall uncertainties. We do not have enough information about the elastic constants to test the crossover form at the tricritical point. Nevertheless, by analogy with 4O.7 we expect that for both $\overline{10}$S5 and $\overline{9}$CB the anisotropy can be ascribed to this mechanism. Indeed, γ and $\nu_\parallel$ are identical in both systems whereas $\nu_\perp$ differs considerably (see Fig. 1). This difference may simply reflect the nonuniversal nature of the crossover behavior. We should also emphasize that Eq. (1) is

TABLE I. Evolution of critical exponents in mixtures approaching the tricritical point.

Material	T_{NA}/T_{NI}	$\alpha = \alpha'$	$\nu_\perp$	$\nu_\parallel$	γ	$\alpha + \nu_\parallel + 2\nu_\perp$
XY		-0.026	0.67 to 0.33	0.67	1.32	2
$\overline{8}$S5	0.936	-0	0.68	0.83	1.53	2.19 ± 0.16
$\overline{9}$S5	0.967	0.22	0.57	0.71	1.31	2.01 ± 0.18
$\overline{8}$CB	0.977	0.31	0.51	0.67	1.26	2.00 ± 0.13
$\overline{10}$S5	0.984	0.45	0.51	0.61	1.10	2.08 ± 0.18
$\overline{9}$CB	0.994	0.53	0.37	0.57	1.10	$1.84^{+0.22}_{-0.14}$
Tricritical	0.87	0.5	0.5 to 0.25	0.5 to 0.25	1	2

strictly empirical. In 9CB especially we find large deviations from Lorentzian behavior over the whole temperature range; typically $c = 0.1$ to 0.25. The transverse scans can be equally well fitted by a Lorentzian raised to the power 1.6. A theoretical prediction for the form of $S(q_\perp)$ in the crossover region is needed.

It has been shown previously[9] that for systems with long nematic ranges both γ and $\nu_\parallel$ are respectively about 0.15 and 0.11 larger than the $d = 3$, $n = 2$ values. At the tricritical points for $\overline{10}$S5 and 9CB we find $\gamma(\text{meas}) - \gamma(\text{theor}) = 0.10 \pm 0.05$ and $\nu_\parallel$ (meas) $- \nu_\parallel$(theor) $= 0.09 \pm 0.04$ over the reduced temperature range $\sim 2 \times 10^{-5}$ to $\sim 10^{-2}$. These discrepancies remain unexplained. The anisotropic hyperscaling relation Eq. (2) holds for all materials measured to date including our tricritical systems. However, averaging over all systems in the literature (excluding $\overline{10}$S5 and 9CB), we find $\alpha + 3\nu_\parallel = 2.36 \pm 0.1$. For $\overline{10}$S5 and 9CB we find as an average $\alpha + 3\nu_\parallel = 2.26 \pm 0.14$. Thus, even at the tricritical point anisotropic rather than isotropic scaling seems to hold. This discrepancy with the theory remains unexplained. Finally, we note that the presently known elastic behavior below T_c is inconsistent with the helium model.

In summary, with this work we have empirically characterized the mass density fluctuations near the N-S_A transition from the critical to tricritical limits. The general trends are consistent with current theory. However, there are persistent quantitative discrepancies which remain unexplained. Finally, only limited elastic-constant data above and below T_{NA} are available, especially in the tricritical region. Such measurements are strongly needed in order to complete the empirical picture.

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